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The crystal and molecular structures of three copper-containing complexes and their activities in mimicking galactose oxidase

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Abstract

The structures of three copper-containing complexes, namely (benzoato-κ 2 O,O′)[(E)-2-({[2-(diethylamino)ethyl]imino}methyl)phenolato-κ 3 N,N′,O]copper(II) dihydrate, [Cu(C 7 H 5 O 2)(C 13 H 19 N 2 O)]·2H 2 O, 1, [(E)-2-({[2-(diethylamino)ethyl]imino}methyl)phenolato-κ 3 N,N′,O](2-phenylacetato-κ 2 O,O′)copper(II), [Cu(C 8 H 7 O 2)(C 13 H 19 N 2 O)], 2, and bis[μ-(E)-2-({[3-(diethylamino)propyl]imino}methyl)phenolato]-κ 4 N,N′,O:O;κ 4 O:N,N′,O-(μ-2-methylbenzoato-κ 2 O:O′)copper(II) perchlorate, [Cu 2 (C 8 H 7 O 2)(C 12 H 17 N 2 O) 2]ClO 4 , 3, have been reported and all have been tested for their activity in the oxidation of d-galactose. The results suggest that, unlike the enzyme galactose oxidase, due to the precipitation of Cu 2 O, this reaction is not catalytic as would have been expected. The structures of 1 and 2 are monomeric, while 3 consists of a dimeric cation and a perchlorate anion [which is disordered over two orientations, with occupancies of 0.64 (4) and 0.36 (4)]. In all three structures, the central Cu atom is five-coordinated in a distorted square-pyramidal arrangment (τ parameter of 0.0932 for 1, 0.0888 for 2, and 0.142 and 0.248 for the two Cu centers in 3). In each species, the environment about the Cu atom is such that the vacant sixth position is open, with very little steric crowding.

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The crystal and molecular structures of three copper-containing complexes and their activities in mimicking galactose oxidase

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The structures of three copper-containing complexes, namely (benzoato-κ^2O,O')[(*E*)-2-({[2-(diethylamino)ethyl]imino}methyl)phenolato-κ^3N,N',O]copper(II) dihydrate, $[Cu(C_7H_5O_2)(C_{13}H_{19}N_2O)]\cdot 2H_2O$, **1**, [(*E*)-2-({[2-(diethylamino)-ethyl]imino}methyl)phenolato-κ^3N,N',O](2-phenylacetato-κ^2O,O')copper(II), $[Cu(C_8H_7O_2)(C_{13}H_{19}N_2O)]$, **2**, and bis[$\mu$-(*E*)-2-({[3-(diethylamino)propyl]imino}-methyl)phenolato]-$\kappa^4N,N',O:O;\kappa^4O:N,N',O$-($\mu$-2-methylbenzoato-$\kappa^2O:O'$)cop-per(II) perchlorate, $[Cu_2(C_8H_7O_2)(C_{12}H_{17}N_2O)_2]ClO_4$, **3**, have been reported and all have been tested for their activity in the oxidation of D-galactose. The results suggest that, unlike the enzyme galactose oxidase, due to the precipitation of Cu_2O, this reaction is not catalytic as would have been expected. The structures of **1** and **2** are monomeric, while **3** consists of a dimeric cation and a perchlorate anion [which is disordered over two orientations, with occupancies of 0.64 (4) and 0.36 (4)]. In all three structures, the central Cu atom is five-coordinated in a distorted square-pyramidal arrangment (τ parameter of 0.0932 for **1**, 0.0888 for **2**, and 0.142 and 0.248 for the two Cu centers in **3**). In each species, the environment about the Cu atom is such that the vacant sixth position is open, with very little steric crowding.

1. Introduction

The coordination chemistry of polynuclear copper(II) complexes with bridging N_2O-donor ligands continues to be actively investigated because of their relevance to a number of areas of importance, including bioinorganic modeling chemistry (Solomon *et al.*, 1996), magnetic properties of polynuclear species (Gatteschi & Sessoli, 2003), catalysis (Kirillov *et al.*, 2005; Tsai *et al.*, 2014), and coordination polymers (Kirillov *et al.*, 2008). Polynuclear complexes containing bridging carboxylate groups are also of current interest due to their biological relevance in many biochemical systems involving mono- and polymetallic active sites (Pecoraro, 1992; Wieghardt, 1989). A particular case is the use of copper complexes which contain very similar coordination ligands (Schiff base derivatives composed of a salicylaldehyde combined with *N*,*N*′-dimethylethane-1,2-diamine) as active catalysts for the copolymerization of cyclohexene oxide (CHO) and CO_2 without cocatalysts (Tsai *et al.*, 2014). Several of these complexes performed satisfactorily to produce polycarbonates with controllable molecular weights and many carbonate linkages.

One system of great interest is galactose oxidase, which is a copper-containing fungal enzyme that catalyzes the oxidation of primary alcohols to their corresponding aldehydes along with the reduction of dioxygen to hydrogen peroxide (Amaral

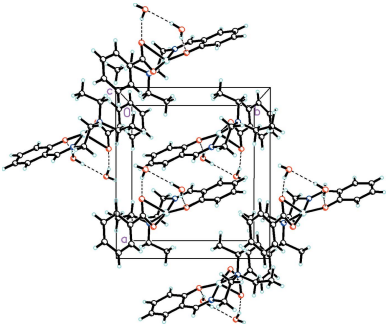
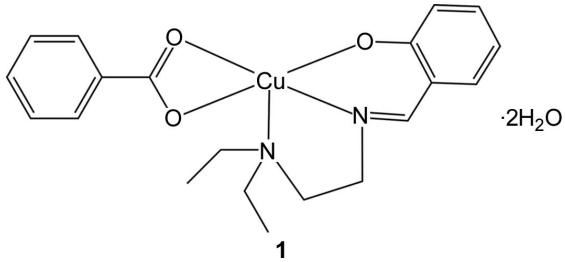


Table 1
Experimental details.

	1	2	3
Crystal data			
Chemical formula	$[Cu(C_7H_5O_2)(C_{13}H_{19}N_2O)]\cdot 2H_2O$	$[Cu(C_8H_7O_2)(C_{13}H_{19}N_2O)]$	$[Cu_2(C_8H_7O_2)(C_{12}H_{17}N_2O)_2]ClO_4$
M_r	439.98	417.98	772.22
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pca2_1$	Orthorhombic, $Pbca$
Temperature (K)	100	100	100
a, b, c (Å)	11.2427 (3), 10.1287 (2), 17.7683 (3)	23.1862 (10), 6.4178 (3), 13.1598 (6)	10.51085 (16), 22.2419 (5), 28.8403 (5)
α, β, γ (°)	90, 92.501 (2), 90	90, 90, 90	90, 90, 90
V (Å^3)	2021.42 (8)	1958.22 (15)	6742.3 (2)
Z	4	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.11	1.14	1.40
Crystal size (mm)	0.35 × 0.23 × 0.18	0.20 × 0.11 × 0.03	0.26 × 0.21 × 0.03
Data collection			
Diffractometer	Rigaku OD SuperNova Dual source diffractometer with an Atlas detector	Rigaku OD SuperNova Dual source diffractometer with an Atlas detector	Rigaku OD SuperNova Dual source diffractometer with an Atlas detector
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2018)	Gaussian (*CrysAlis PRO*; Rigaku OD, 2018)	Gaussian (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.474, 1.000	0.684, 1.000	0.614, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	51132, 13125, 10770	46196, 11501, 7093	154652, 22070, 12413
R_{int}	0.030	0.089	0.090
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.928	0.928	0.933
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.076, 1.07	0.056, 0.121, 1.04	0.053, 0.135, 1.04
No. of reflections	13125	11501	22070
No. of parameters	270	245	467
No. of restraints	6	1	44
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.57, −0.60	1.20, −1.04	1.13, −1.11
Absolute structure	–	Flack x determined using 1976 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)	–
Absolute structure parameter	–	−0.035 (10)	–

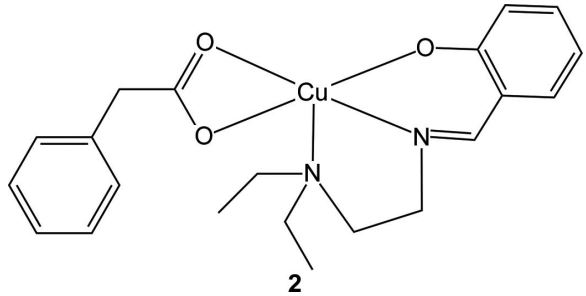
Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

et al., 1963; Whittaker, 1994). The crystal structure of the inactive Cu^{II} form of galactose oxidase (Ito *et al.*, 1991, 1994) shows that the enzyme contains a Cu atom bound to two histidine N atoms, two tyrosine O atoms and a water molecule in a distorted square-pyramidal environment at the active site of the enzyme.



1

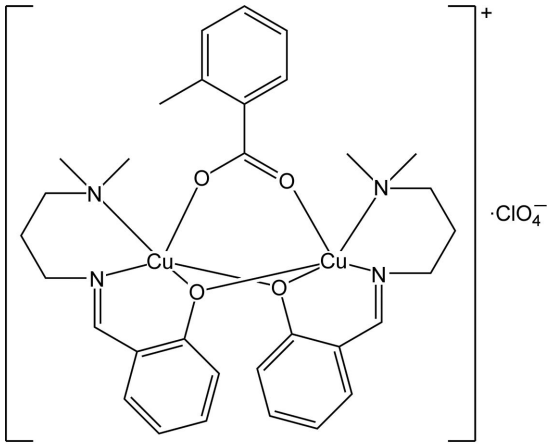
The use of mass spectrometry has been reported in a study of the oxidation of D-galactose (Gal) by Cu^{II} complexes of a series of tridentate Schiff base ligands in alcohol/NaOH solutions (Butcher *et al.*, 2014). The change in the color of the solutions from blue–green to yellow and the appearance of a negative-ion electrospray mass spectral peak at m/z = 195 [Oxidized Gal + OH] showed that the copper complexes had oxidized the galactose while being reduced to a Cu^{I} species.



2

Compounds of the formula Cu*LX*, where *L* is a tridentate Schiff base ligand formed by the reaction of salicylaldehyde and an amine, $NH_2(CH_2)_nNR_2$, where n = 2 or 3, R = CH_3 or C_2H_5, and *X* is benzoic acid (for **1**), phenylacetic acid (for **2**), or 2-methylbenzoic acid (for **3**), have been synthesized and tested for their activity, *c*. There have been previous reports of similar copper complexes with carboxylic acids, but in no cases were these complexes tested for their activity in the oxidation of D-galactose (Bhowmik *et al.*, 2013, 2014; Gönül *et al.*, 2018;

Wang & You, 2007; Xanthopoulos *et al.*, 1992, 1993*a*,*b*,*c*, 2002), although very similar compounds have been shown to be active as efficient catalysts for the copolymerization of carbon dioxide and cyclohexene oxide (Tsai *et al.*, 2014). The reactions of these compounds with D-galactose in CH_3CN/NaOH solutions were investigated using electrospray mass spectrometry.



3

2. Experimental

All reagents were purchased from commercial sources and were used as supplied. UV–Vis spectra in the range 400–900 nm were obtained using a Shimadzu UV-2401 spectrophotometer. Solid-state spectra were measured as Nujol mulls on filter paper. ESI mass spectra were obtained using a Micromass VG quattro-2 quadrupole mass spectrometer (Altringham, UK), utilizing a Z-spray ion source. The solutions used for mass spectral measurements contained 0.005 *M* solutions of the copper compounds in 50:50 CH_3CN/H_2O and 50:50 CH_3CN/0.01 *M* NaOH.

2.1. Synthesis and crystallization

Salicylaldehyde (0.025 mol) was refluxed with the appropriate amine (0.025 mol) in methanol (50 ml) for 30 min. After cooling to room temperature, triethylamine (2.5 ml) was added to the solution. A solution of Cu(acidate)$_2$·H_2O (0.025 mol) [acidate = benzoate, 2-methylbenzoate or phenylacetate] dissolved in methanol (200 ml) was added to the Schiff base solution and the resulting solution was refluxed for 30 min. The solutions were filtered and the products were allowed to crystallize slowly from the solutions (in all three cases, this resulted in X-ray-quality crystals). Yields of about 60% were obtained for all samples.

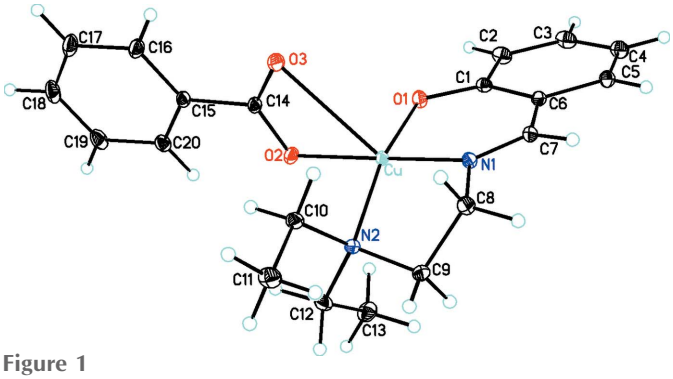


Figure 1
The molecular structure of **1**, showing the atom labeling. Displacement ellipsoids are drawn at the 30% probability level.

Table 2
Positive- and negative-ion electrospray mass spectra of Cu*LX* plus D-galactose (Gal) in CH_3CN/H_2O solution.

The mass spectral peaks (*m*/*z*) for CuL^+ and X^- appear for each compound. These data indicate the dissociation scheme implied by the peak assignments.

Assigned peaks (*m*/*z*)	Benzoate, **1**	Phenylacetate, **2**	2-Methylbenzoate, **3**
CuL^+	268	282	282
$(L + H)^+$	207	221	221
$(Gal + Na)^+$	203	203	203
$(Oxidized\ Gal + OH)^-$	195	195	195
$(Gal - H)^-$	179	179	179
X^-	121	135	135

2.2. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 1. In each case, the H atoms were refined with C—H distances varying from 0.95 to 0.99 Å and atomic displacement parameters of $1.2U_{eq}$(C) or $1.5U_{eq}$(CH_3). In **1**, the water H atoms were refined isotropically, while for **3**, the perchlorate O atoms were disordered and modelled with two equivalent conformations having occupancies of 0.64 (3) and 0.36 (3).

3. Results and discussion

3.1. Spectra

In the UV–Vis spectra of the three complexes, the benzoate (in **1**), phenylacetate (in **2**) and *o*-toluate dimer (in **3**) have broad peaks (620, 615 and 720 nm, respectively) in the visible region of the spectra, which is consistent with the presence of five-coordinate copper(II). The longer wavelength seen for **3** indicates the presence a weaker ligand field for this compound.

3.2. Mass spectra

The positive- and negative-ion mass spectra of the three compounds with D-galactose (Gal) were run in CH_3CN/H_2O solutions (Table 2). The data indicates the following dissociation:

$$CuLX \rightarrow CuL^+ + X^-.$$

The main peaks in the positive-ion mass spectra are $[CuL]^+$ (*m*/*z* = 268 or 282), $[Gal + Na]^+$ (*m*/*z* = 203) and $[L + H]^+$ (*m*/*z* = 207 or 221). The main peaks in the negative-ion mass spectra are $[X]^-$ (for benzoate, *m*/*z* = 121, and for *o*-toluate and phenylacetate, *m*/*z* = 135) and $[Gal - H]^-$ (*m*/*z* = 179). In a solution of CH_3CN/NaOH over time, the color of the solutions

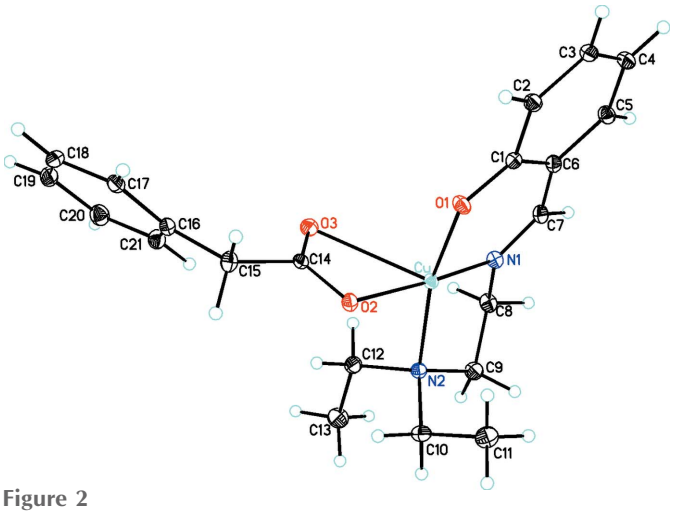


Figure 2
The molecular structure of **2**, showing the atom labeling. Displacement ellipsoids are drawn at the 30% probability level.

change from blue–green to yellow with the precipitation of orange Cu_2O.

$$2CuL^{+} + Gal + 2OH^{-} \rightarrow Cu_2O + \text{Oxidized Gal} + 2LH + H_2O.$$

In the negative-ion mass spectra where the ratio of Cu*LX* to Gal is 2:1, the two main peaks are [Oxidized Gal + OH]$^-$ (m/z = 195) and X^- (for benzoate, m/z = 121, and for *o*-toluate and phenylacetate, m/z = 135). When the amount of Gal relative to Cu*LX* is increased, the mass spectral data indicates the presence of both Gal (m/z = 179) and its oxidized product (m/z = 195). This suggests that, unlike the enzyme galactose oxidase, this reaction is not catalytic, as would have been expected due to the precipitation of Cu_2O.

3.3. Structural results

The structural results for the three compounds will first be discussed individually and then comparisons made. The first structure, *i.e.* **1**, consists of a five-coordinate (4 + 1) copper complex, together with two water solvent molecules (Fig. 1). The coordination sphere of the Cu atom is made up of a tridentate Schiff base ligand resulting from the condensation of *N*,*N*-diethylethane-1,2-diamine and salicylaldehyde, as well as a benzoate anion coordinating in an asymmetric bidentate mode, resulting in a square-pyramidal five-coordinate complex (τ = 0.0932; Addison *et al.*, 1984). The basal plane consists of atoms O1, N1 and N2 of the Schiff base and O2 of the benzoate anion [the r.m.s. deviation of the fitted atoms is 0.173 Å, with the Cu atom displaced by 0.0667 (3) Å from the basal plane]. The Cu—O and Cu—N bond lengths in the basal plane are 1.9183 (5)/1.9550 (6) and 1.9246 (6)/2.0863 (6) Å. Both the former and latter distances are not equivalent, with the Cu—O(Schiff) bond length being shorter than the Co—O(benzoate) bond length. A search of the Cambridge Structural Database (CSD; Groom *et al.*, 2016) for Cu–Schiff base complexes also containing coordinated benzoate derivatives gave 39 hits with an average Cu—O(Schiff) bond length of 1.923 (19) Å and an average Cu—O(benzoate) bond length of 1.977 (18) Å, showing a similar difference in such parameters. Similarly, the Cu—N(imine) bond length is significantly shorter than the Cu—N(amine) bond length, as is commonly found in such complexes (Egekenze *et al.*, 2018). The apical Cu—O bond length is 2.7360 (6) Å and the plane of the carboxylate group is almost perpendicular to the square-planar basal plane [dihedral angle between planes = 82.73 (4)°].

The structure of **2** is similar to that of **1**, with the major difference being the substitution of a phenylacetate anion for the benzoate anion. The resulting structure is a square-pyramidal (τ = 0.0888; Addison *et al.*, 1984) five-coordinate (4 + 1) copper complex containing the same tridentate Schiff base ligand as **1**, with the phenylacetate anion coordinating in an asymmetric bidentate fashion (Fig. 2). The basal plane consists of atoms O1, N1 and N2 of the Schiff base and atom O2 of phenylacetate [the r.m.s. deviation of the atoms is 0.180 Å and the Cu atom is displaced by 0.0510 (1) Å from the basal plane]. The Cu—O and Cu—N bond lengths in the basal plane are 1.909 (2)/1.957 (2) and 1.923 (2)/2.068 (2) Å, respectively, and show similar trends as discussed for **1**. The apical Cu—O bond length is 2.604 (2) Å and the plane of the carboxylate group is almost perpendicular to the square-planar basal plane [dihedral angle between planes = 82.95 (17)°].

The structures **1** and **2** contain the same Schiff base ligand, namely (*E*)-2-({[2-(diethylamino)ethyl]imino}methyl)phenolate. A search of the CSD for copper complexes containing either this ligand or an analogous ligand containing the dimethylamino group, along with coordinated carboxylate anions, gave 26 hits, of which those with CSD refcodes

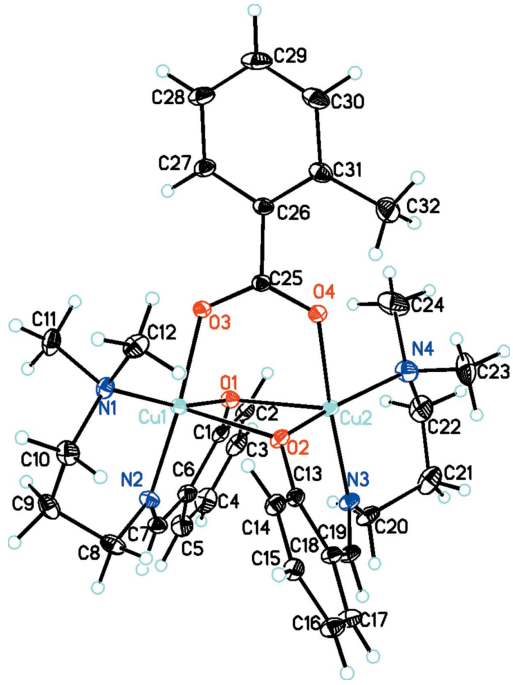


Figure 3
The cation in **3**, showing the atom labeling. Displacement ellipsoids are drawn at the 30% probability level.

Table 3
Hydrogen-bond geometry (Å, °) for (2).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8B···O2^{i}	0.99	2.37	3.260 (4)	149
C9—H9B···O3^{ii}	0.99	2.28	3.172 (4)	149
C12—H12B···O2	0.99	2.64	3.183 (4)	115

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y+1, z+\frac{1}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for **3**.

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10B···O13A^{i}	0.99	2.69	3.418 (12)	130
C10—H10B···O13B^{i}	0.99	2.44	3.242 (14)	138
C11—H11B···O13A^{ii}	0.98	2.65	3.148 (8)	111
C11—H11C···O3	0.98	2.48	3.039 (2)	116
C12—H12B···O3	0.98	2.34	2.866 (3)	113
C14—H14A···O14A^{i}	0.95	2.49	3.127 (10)	124
C19—H19A···O11A	0.95	2.26	3.159 (12)	158
C20—H20B···O12A	0.99	2.63	3.606 (13)	169
C24—H24B···O4	0.98	2.29	2.807 (3)	112

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

IKAXEZ (Bhowmik *et al.*, 2014), LECCAX (Xanthopoulos *et al.*, 1993*b*), LOJXEN (Yin *et al.*, 1998), NESYAO and NESYES (Gönül *et al.*, 2018), PIFHUH (Xanthopoulos *et al.*, 1993*c*), WOGSOB (Lin *et al.*, 2008) and XICGUM (Wang & You, 2007) have the closest similarity in that they are discrete mononuclear complexes. The metrical parameters in these complexes are similar to those found in **1** and **2**, and the carboxylate group is usually coordinated in a similar asymmetrical fashion with one longer and one shorter Cu—O bond length.

The structure of **3** consists of a dimeric bis[μ-(*E*)-2-({[3-(diethylamino)propyl]imino}methyl)phenolato](μ-2-methylbenzoato)copper(II) cation and a perchlorate anion. In the cation, the ligands are an anionic Schiff base resulting from the condensation of *N*,*N*-dimethylpropane-1,3-diamine with salicyladehyde, as well as the anion of 3-methylbenzoic acid. Each Schiff base bridges both Cu^{2+} ions in a μ-*O*:*O*-fashion, while the 2-methylbenzoate anion bridges both Cu^{2+} ions in a μ-*O*:*O*′-fashion (Fig. 3). The perchlorate anion is disordered over two orientations sharing a common central Cl atom, with occupancies of 0.64 (4) and 0.36 (4). Both Cu atoms are in a distorted square-pyramidal five-coordinate geometry, with Cu2 being significantly more distorted than Cu1 (τ = 0.142 for Cu1 and 0.248 for Cu2; Addison *et al.*, 1984), and with a Cu1···Cu2 separation of 3.0155 (3) Å. For Cu1, the basal plane consists of atoms N1, N2 and O1 of the Schiff base and atom O3 of the 2-methylbenzoate anion, with O2 from the other Schiff base being the apical donor [the r.m.s. deviation of the fitted atoms of the basal plane is 0.0545 Å and atom Cu1 is displaced by 0.1812 (8) Å from this plane], while for Cu2, with a greater distortion from square-planar geometry, the basal plane consists of atoms N3, N4 and O2 of the Schiff base and atom O4 of the 2-methylbenzoate anion, with O1 from the other Schiff base being the apical donor [the r.m.s. deviation of the fitted atoms of the basal plane is 0.1258 Å and atom Cu2 is displaced by 0.2321 (9) Å from this plane]. For the two square-pyramidal fragments, the Cu—O apical distances are 2.2935 (13) and 2.3053 (14) Å. These distances are much shorter and less asymmetric than those observed in the two monomeric square-pyramidal complexes already discussed. However, they are considerably longer than the average Cu—O distance observed for benzoate derivatives bridging two Cu atoms, such that each Cu atom is only attached to one of the two carboxylate O atoms and each O atom is only attached to

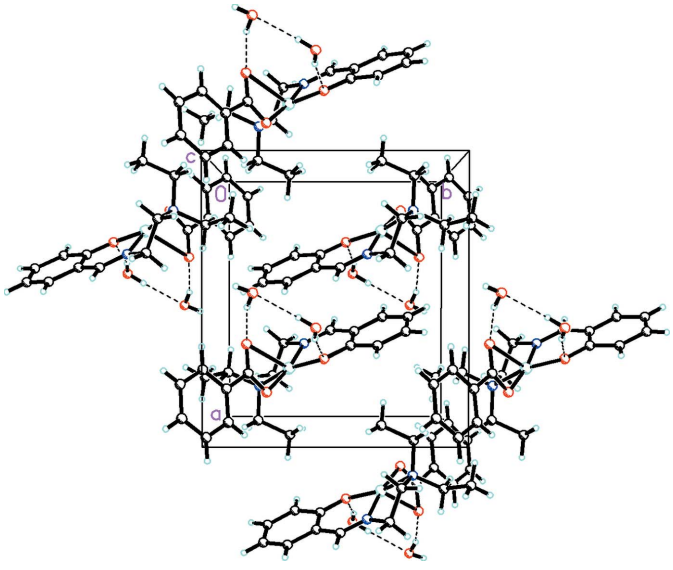


Figure 4
Packing diagram for **1**, viewed along the *c* axis, showing the π–π stacking and O—H···O hydrogen bonding (indicated by dashed bonds) involving the water molecules.

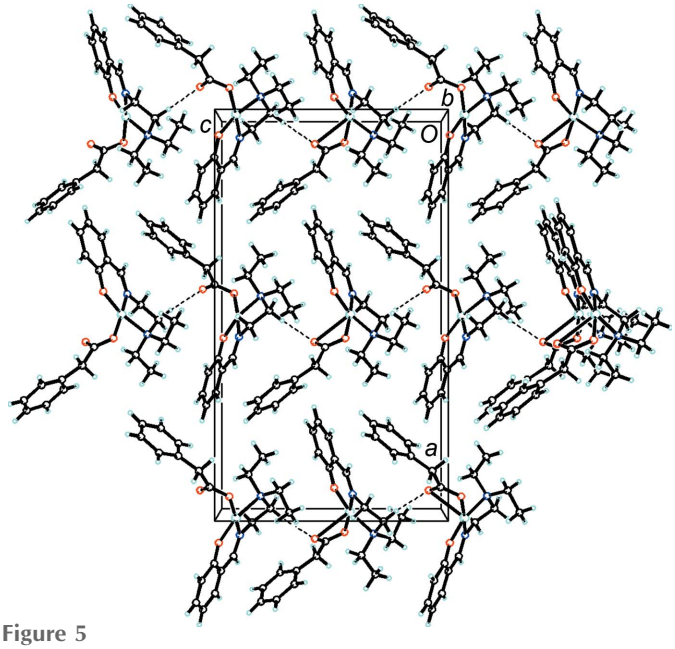


Figure 5
Packing diagram for **2**, viewed along the *b* axis, showing the C—H···O interactions (indicated by dashed bonds) linking the molecules into a zigzag ribbon in the *c* direction.

a single Cu atom [4330 observations with average Cu—O distances of 1.97 (4) and 1.98 (5) Å]

A search of the CSD for dinuclear copper complexes containing similar Schiff bases with a μ-*O*:*O*′-carboxylate coordination gave a number of hits [CSD refcodes PIBXOU (Chiari *et al.* 1993), CESTAW (You *et al.*, 2006), KEZCUO (Dey *et al.*, 2007), PIZTUP (Tsai *et al.*, 2014), TIFVIP (Bhowmik *et al.*, 2013), and VALCEQ (Biswas *et al.*, 2010)] and, in each example, the metrical parameters for the Cu coordination spheres are very similar to those observed in the title complexes.

In assessing the relevance of these compounds as potential catalysts, it should be noted that, in each case, these structures contain a five-coordinated Cu centre in a slightly distorted square-pyramidal geometry (τ = 0.0932 for **1**, 0.0888 for **2**, and 0.142 and 0.248 for **3**) and thus each has a potentially accessible site for catalytic activity. The closest intermolecular contacts involving the Cu atom are 3.717 Å to C5 at ($-x+1$, $-y+1$, $-z+1$) for **1**, 3.243 Å to H8*B* at (x, $y+1$, z) for **2**, and 3.721 Å to H8*B* at ($x-\frac{1}{2}$, y, $-z+\frac{1}{2}$) and 4.087 Å to H23*C* at ($-x+1$, $-y+2$, z) for **3**, thus showing how available these sites are.

3.4. Supramolecular results

In **1**, there are two H_2O solvent molecules which are involved in both hydrogen bonding to both each other and atoms O2 and O3 (Table 3), forming a chain in the *b* direction, as shown in Fig. 4. The complex is involved in π–π stacking interactions between the Cu/O1/C1/C6/C7/N1 chelate ring (*Cg*1) and the arene ring of an adjoining molecule [*Cg*1···*Cg*2 = 3.6826 (4) Å, *Cg*···perpendicular distances = 3.1948 (2) and 3.2573 (3) Å, and slippage = 1.718 Å; *Cg*2 is the centroid of the C1–C6 ring; symmetry code on *Cg*2: $-x+1$, $-y+1$, $-z+1$]. Interestingly, this interaction between molecules is on the opposite side of the vacant sixth coordination sites of the two Cu atoms involved and this does not hinder access to this site.

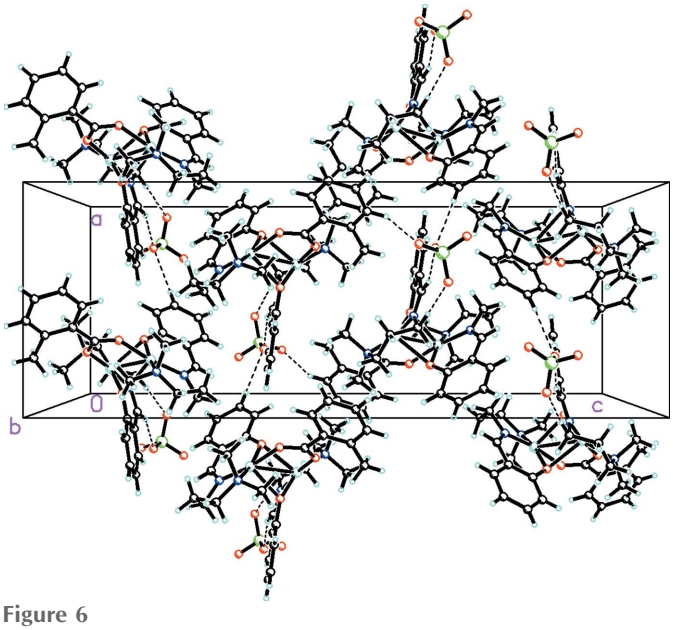


Figure 6
Packing diagram for **3**, viewed along the *b* axis, showing how the cations and anions are linked into a three-dimensional array *via* C—H···O interactions (indicated by dashed bonds) involving the perchlorate anion.

In **2**, the packing diagram shows that the molecules are linked into zigzag chains in the *c* direction by C—H···O interactions (Table 4 and Fig. 5). There are no π–π or C—H···π interactions.

For **3**, there are no π–π or C—H···π interactions and the central O atoms (O1–O4) are sterically hindered from participating in C—H···O interactions. Thus, the only interactions affecting the packing involve weak C—H···O interactions involving the O11*A*/O12*A*/O13*A* perchlorate anion, which link the cations and anions into a complex three-dimensional array, as seen in the packing diagram (Fig. 6).

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supporting information

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The crystal and molecular structures of three copper-containing complexes and their activities in mimicking galactose oxidase

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Computing details

For all structures, data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(Benzoato-κ^2O,O')[(*E*)-2-({[2-(diethylamino)ethyl]imino}methyl)phenolato-κ^3N,N',O]copper(II) dihydrate (1)

Crystal data

$[Cu(C_7H_5O_2)(C_{13}H_{19}N_2O)]\cdot 2H_2O$
$M_r = 439.98$
Monoclinic, $P2_1/c$
$a = 11.2427$ (3) Å
$b = 10.1287$ (2) Å
$c = 17.7683$ (3) Å
$\beta = 92.501$ (2)°
$V = 2021.42$ (8) Å^3
$Z = 4$
$F(000) = 924$
$D_x = 1.446$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 20474 reflections
$\theta = 3.8$–40.9°
$\mu = 1.11$ mm^{-1}
$T = 100$ K
Multi-faceted prism, blue
0.35 × 0.23 × 0.18 mm

Data collection

Rigaku OD SuperNova Dual source diffractometer with an Atlas detector
Radiation source: micro-focus sealed X-ray tube
Detector resolution: 10.6501 pixels mm^{-1}
ω scans
Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2018)
$T_{min} = 0.474$, $T_{max} = 1.000$
51132 measured reflections
13125 independent reflections
10770 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 41.3°$, $\theta_{min} = 3.5°$
$h = -20\rightarrow20$
$k = -18\rightarrow18$
$l = -25\rightarrow32$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.076$
$S = 1.07$
13125 reflections
270 parameters
6 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 0.3747P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu	0.23818 (2)	0.69525 (2)	0.47778 (2)	0.01137 (2)
O1	0.27766 (5)	0.54601 (5)	0.41727 (3)	0.01650 (9)
O2	0.15402 (5)	0.78344 (6)	0.39331 (3)	0.01670 (9)
O3	0.33453 (5)	0.86472 (6)	0.37715 (3)	0.01897 (10)
O1W	0.52308 (7)	0.83109 (7)	0.28425 (4)	0.02636 (13)
H1W1	0.4716 (12)	0.8598 (15)	0.3113 (8)	0.034 (4)*
H1W2	0.5502 (16)	0.8967 (16)	0.2641 (10)	0.060 (5)*
O2W	0.39643 (9)	0.57738 (7)	0.27758 (4)	0.03167 (16)
H2W1	0.3575 (13)	0.5822 (15)	0.3162 (8)	0.037 (4)*
H2W2	0.4310 (14)	0.6492 (14)	0.2765 (9)	0.042 (4)*
N1	0.33000 (6)	0.63419 (6)	0.56489 (3)	0.01338 (9)
N2	0.16538 (6)	0.82506 (6)	0.55446 (3)	0.01380 (9)
C1	0.32672 (6)	0.43555 (7)	0.44259 (4)	0.01414 (10)
C2	0.32873 (8)	0.32474 (8)	0.39411 (5)	0.02019 (13)
H2A	0.294165	0.331522	0.344513	0.024*
C3	0.38021 (8)	0.20647 (8)	0.41763 (6)	0.02339 (15)
H3A	0.378582	0.133178	0.384235	0.028*
C4	0.43441 (8)	0.19302 (7)	0.48948 (6)	0.02259 (15)
H4A	0.471294	0.112327	0.504607	0.027*
C5	0.43329 (8)	0.29896 (7)	0.53786 (5)	0.01865 (12)
H5A	0.469865	0.290767	0.586855	0.022*
C6	0.37906 (6)	0.41938 (7)	0.51635 (4)	0.01382 (10)
C7	0.38029 (6)	0.52083 (7)	0.57282 (4)	0.01411 (10)
H7A	0.421362	0.502782	0.619548	0.017*
C8	0.32821 (7)	0.72459 (8)	0.62904 (4)	0.01648 (11)
H8A	0.383817	0.799046	0.622365	0.020*
H8B	0.351197	0.678039	0.676465	0.020*
C9	0.20140 (7)	0.77360 (8)	0.63053 (4)	0.01702 (12)
H9A	0.147997	0.700558	0.644253	0.020*
H9B	0.195502	0.844521	0.668525	0.020*
C10	0.21916 (7)	0.95742 (7)	0.54046 (4)	0.01689 (12)
H10A	0.188508	0.989212	0.490618	0.020*
H10B	0.306310	0.946107	0.537607	0.020*
C11	0.19639 (9)	1.06407 (8)	0.59850 (5)	0.02305 (15)
H11A	0.226691	1.148804	0.580836	0.035*
H11B	0.237177	1.040824	0.646542	0.035*
H11C	0.110635	1.071227	0.605459	0.035*
C12	0.03368 (7)	0.82973 (8)	0.54397 (5)	0.01943 (13)
H12A	0.012276	0.883028	0.498678	0.023*

H12B	0.000355	0.874369	0.587918	0.023*
C13	−0.02251 (8)	0.69370 (9)	0.53516 (6)	0.02444 (15)
H13A	−0.109103	0.702796	0.528447	0.037*
H13B	0.008651	0.649662	0.491031	0.037*
H13C	−0.003276	0.640999	0.580316	0.037*
C14	0.22685 (7)	0.85663 (7)	0.35854 (4)	0.01419 (10)
C15	0.17491 (7)	0.93920 (7)	0.29497 (4)	0.01484 (11)
C16	0.24644 (8)	1.02998 (8)	0.25883 (4)	0.01974 (13)
H16A	0.328766	1.035916	0.272873	0.024*
C17	0.19839 (10)	1.11179 (9)	0.20249 (5)	0.02590 (17)
H17A	0.247678	1.173462	0.178319	0.031*
C18	0.07821 (10)	1.10309 (9)	0.18165 (5)	0.02722 (18)
H18A	0.045041	1.159443	0.143495	0.033*
C19	0.00625 (9)	1.01191 (10)	0.21660 (5)	0.02489 (16)
H19A	−0.075915	1.005821	0.202140	0.030*
C20	0.05468 (8)	0.92951 (8)	0.27283 (4)	0.01896 (12)
H20A	0.005618	0.866548	0.296135	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.01340 (4)	0.01114 (3)	0.00955 (3)	0.00143 (3)	0.00042 (2)	0.00089 (2)
O1	0.0219 (2)	0.0150 (2)	0.01244 (19)	0.00371 (18)	−0.00101 (17)	−0.00138 (16)
O2	0.0184 (2)	0.0180 (2)	0.0136 (2)	0.00053 (18)	−0.00005 (17)	0.00472 (16)
O3	0.0171 (2)	0.0228 (2)	0.0169 (2)	0.0019 (2)	−0.00086 (18)	0.00397 (19)
O1W	0.0273 (3)	0.0280 (3)	0.0243 (3)	0.0005 (3)	0.0065 (2)	0.0045 (2)
O2W	0.0522 (5)	0.0228 (3)	0.0208 (3)	0.0024 (3)	0.0110 (3)	−0.0015 (2)
N1	0.0154 (2)	0.0137 (2)	0.01093 (19)	0.00220 (18)	−0.00039 (17)	−0.00069 (16)
N2	0.0142 (2)	0.0133 (2)	0.0142 (2)	0.00149 (18)	0.00314 (18)	0.00104 (17)
C1	0.0148 (3)	0.0126 (2)	0.0152 (2)	−0.0006 (2)	0.0022 (2)	−0.00182 (19)
C2	0.0212 (3)	0.0175 (3)	0.0219 (3)	−0.0010 (2)	0.0017 (3)	−0.0070 (2)
C3	0.0236 (4)	0.0142 (3)	0.0329 (4)	−0.0017 (3)	0.0062 (3)	−0.0075 (3)
C4	0.0245 (4)	0.0112 (2)	0.0327 (4)	0.0017 (2)	0.0079 (3)	0.0017 (3)
C5	0.0209 (3)	0.0128 (2)	0.0225 (3)	0.0027 (2)	0.0043 (3)	0.0042 (2)
C6	0.0150 (3)	0.0113 (2)	0.0153 (2)	0.0008 (2)	0.0027 (2)	0.00123 (19)
C7	0.0149 (3)	0.0148 (2)	0.0126 (2)	0.0018 (2)	0.0004 (2)	0.00160 (19)
C8	0.0193 (3)	0.0177 (3)	0.0123 (2)	0.0021 (2)	−0.0010 (2)	−0.0027 (2)
C9	0.0204 (3)	0.0184 (3)	0.0126 (2)	0.0026 (2)	0.0042 (2)	0.0003 (2)
C10	0.0183 (3)	0.0130 (2)	0.0198 (3)	0.0000 (2)	0.0056 (2)	−0.0008 (2)
C11	0.0270 (4)	0.0181 (3)	0.0243 (3)	−0.0015 (3)	0.0043 (3)	−0.0066 (3)
C12	0.0139 (3)	0.0198 (3)	0.0248 (3)	0.0024 (2)	0.0038 (2)	0.0009 (2)
C13	0.0206 (3)	0.0264 (4)	0.0263 (4)	−0.0059 (3)	0.0004 (3)	0.0052 (3)
C14	0.0186 (3)	0.0139 (2)	0.0101 (2)	0.0031 (2)	0.0004 (2)	0.00105 (18)
C15	0.0200 (3)	0.0148 (2)	0.0097 (2)	0.0042 (2)	0.0003 (2)	0.00078 (19)
C16	0.0270 (4)	0.0176 (3)	0.0146 (3)	0.0018 (3)	0.0011 (3)	0.0038 (2)
C17	0.0419 (5)	0.0192 (3)	0.0168 (3)	0.0050 (3)	0.0027 (3)	0.0063 (2)
C18	0.0429 (5)	0.0236 (4)	0.0148 (3)	0.0152 (4)	−0.0030 (3)	0.0031 (3)
C19	0.0284 (4)	0.0287 (4)	0.0171 (3)	0.0129 (3)	−0.0048 (3)	−0.0009 (3)

C20	0.0205 (3)	0.0219 (3)	0.0144 (3)	0.0065 (3)	−0.0005 (2)	0.0002 (2)

Geometric parameters (Å, º)

Cu—O1	1.9183 (5)	C8—C9	1.5110 (11)
Cu—N1	1.9246 (6)	C8—H8A	0.9900
Cu—O2	1.9550 (6)	C8—H8B	0.9900
Cu—N2	2.0863 (6)	C9—H9A	0.9900
Cu—O3	2.7360 (6)	C9—H9B	0.9900
O1—C1	1.3178 (9)	C10—C11	1.5228 (11)
O2—C14	1.2828 (9)	C10—H10A	0.9900
O3—C14	1.2437 (10)	C10—H10B	0.9900
O1W—H1W1	0.821 (12)	C11—H11A	0.9800
O1W—H1W2	0.820 (14)	C11—H11B	0.9800
O2W—H2W1	0.831 (12)	C11—H11C	0.9800
O2W—H2W2	0.825 (13)	C12—C13	1.5210 (12)
N1—C7	1.2849 (9)	C12—H12A	0.9900
N1—C8	1.4630 (9)	C12—H12B	0.9900
N2—C12	1.4850 (10)	C13—H13A	0.9800
N2—C9	1.4881 (10)	C13—H13B	0.9800
N2—C10	1.4960 (9)	C13—H13C	0.9800
C1—C2	1.4156 (10)	C14—C15	1.5029 (9)
C1—C6	1.4225 (10)	C15—C20	1.3947 (11)
C2—C3	1.3870 (12)	C15—C16	1.3963 (11)
C2—H2A	0.9500	C16—C17	1.3904 (12)
C3—C4	1.3970 (15)	C16—H16A	0.9500
C3—H3A	0.9500	C17—C18	1.3881 (16)
C4—C5	1.3754 (12)	C17—H17A	0.9500
C4—H4A	0.9500	C18—C19	1.3917 (15)
C5—C6	1.4089 (10)	C18—H18A	0.9500
C5—H5A	0.9500	C19—C20	1.3941 (11)
C6—C7	1.4359 (10)	C19—H19A	0.9500
C7—H7A	0.9500	C20—H20A	0.9500
O1—Cu—N1	93.92 (2)	N2—C9—C8	108.59 (6)
O1—Cu—O2	92.62 (2)	N2—C9—H9A	110.0
N1—Cu—O2	171.44 (3)	C8—C9—H9A	110.0
O1—Cu—N2	165.85 (2)	N2—C9—H9B	110.0
N1—Cu—N2	83.64 (2)	C8—C9—H9B	110.0
O2—Cu—N2	91.31 (2)	H9A—C9—H9B	108.4
O1—Cu—O3	91.16 (2)	N2—C10—C11	116.23 (6)
N1—Cu—O3	120.89 (2)	N2—C10—H10A	108.2
O2—Cu—O3	53.40 (2)	C11—C10—H10A	108.2
N2—Cu—O3	102.08 (2)	N2—C10—H10B	108.2
C1—O1—Cu	125.54 (5)	C11—C10—H10B	108.2
C14—O2—Cu	109.64 (5)	H10A—C10—H10B	107.4
C14—O3—Cu	73.97 (4)	C10—C11—H11A	109.5
H1W1—O1W—H1W2	104.6 (15)	C10—C11—H11B	109.5

H2W1—O2W—H2W2	103.5 (14)	H11A—C11—H11B	109.5
C7—N1—C8	119.66 (6)	C10—C11—H11C	109.5
C7—N1—Cu	126.40 (5)	H11A—C11—H11C	109.5
C8—N1—Cu	113.60 (5)	H11B—C11—H11C	109.5
C12—N2—C9	110.82 (6)	N2—C12—C13	113.04 (7)
C12—N2—C10	111.01 (6)	N2—C12—H12A	109.0
C9—N2—C10	111.65 (6)	C13—C12—H12A	109.0
C12—N2—Cu	110.82 (5)	N2—C12—H12B	109.0
C9—N2—Cu	105.87 (4)	C13—C12—H12B	109.0
C10—N2—Cu	106.45 (4)	H12A—C12—H12B	107.8
O1—C1—C2	118.88 (7)	C12—C13—H13A	109.5
O1—C1—C6	124.23 (6)	C12—C13—H13B	109.5
C2—C1—C6	116.89 (7)	H13A—C13—H13B	109.5
C3—C2—C1	121.27 (8)	C12—C13—H13C	109.5
C3—C2—H2A	119.4	H13A—C13—H13C	109.5
C1—C2—H2A	119.4	H13B—C13—H13C	109.5
C2—C3—C4	121.28 (7)	O3—C14—O2	122.98 (6)
C2—C3—H3A	119.4	O3—C14—C15	120.33 (7)
C4—C3—H3A	119.4	O2—C14—C15	116.63 (7)
C5—C4—C3	118.66 (8)	C20—C15—C16	119.15 (7)
C5—C4—H4A	120.7	C20—C15—C14	120.86 (7)
C3—C4—H4A	120.7	C16—C15—C14	119.96 (7)
C4—C5—C6	121.43 (8)	C17—C16—C15	120.67 (9)
C4—C5—H5A	119.3	C17—C16—H16A	119.7
C6—C5—H5A	119.3	C15—C16—H16A	119.7
C5—C6—C1	120.43 (7)	C18—C17—C16	119.82 (9)
C5—C6—C7	116.04 (7)	C18—C17—H17A	120.1
C1—C6—C7	123.53 (6)	C16—C17—H17A	120.1
N1—C7—C6	124.89 (6)	C17—C18—C19	120.08 (8)
N1—C7—H7A	117.6	C17—C18—H18A	120.0
C6—C7—H7A	117.6	C19—C18—H18A	120.0
N1—C8—C9	105.33 (6)	C18—C19—C20	120.04 (9)
N1—C8—H8A	110.7	C18—C19—H19A	120.0
C9—C8—H8A	110.7	C20—C19—H19A	120.0
N1—C8—H8B	110.7	C19—C20—C15	120.23 (8)
C9—C8—H8B	110.7	C19—C20—H20A	119.9
H8A—C8—H8B	108.8	C15—C20—H20A	119.9

Cu—O1—C1—C2	167.40 (5)	C12—N2—C10—C11	69.58 (9)
Cu—O1—C1—C6	−12.80 (10)	C9—N2—C10—C11	−54.64 (9)
O1—C1—C2—C3	179.39 (8)	Cu—N2—C10—C11	−169.73 (6)
C6—C1—C2—C3	−0.42 (11)	C9—N2—C12—C13	−71.87 (8)
C1—C2—C3—C4	−1.45 (13)	C10—N2—C12—C13	163.45 (7)
C2—C3—C4—C5	1.69 (13)	Cu—N2—C12—C13	45.36 (8)
C3—C4—C5—C6	−0.04 (12)	Cu—O3—C14—O2	−0.92 (6)
C4—C5—C6—C1	−1.84 (11)	Cu—O3—C14—C15	176.22 (6)
C4—C5—C6—C7	177.93 (7)	Cu—O2—C14—O3	1.32 (9)
O1—C1—C6—C5	−177.78 (7)	Cu—O2—C14—C15	−175.93 (5)

C2—C1—C6—C5	2.02 (10)	O3—C14—C15—C20	179.00 (7)
O1—C1—C6—C7	2.47 (11)	O2—C14—C15—C20	−3.67 (10)
C2—C1—C6—C7	−177.73 (7)	O3—C14—C15—C16	−3.00 (10)
C8—N1—C7—C6	174.37 (7)	O2—C14—C15—C16	174.33 (7)
Cu—N1—C7—C6	1.60 (11)	C20—C15—C16—C17	1.29 (11)
C5—C6—C7—N1	−176.20 (7)	C14—C15—C16—C17	−176.75 (7)
C1—C6—C7—N1	3.56 (11)	C15—C16—C17—C18	−0.21 (13)
C7—N1—C8—C9	−133.03 (7)	C16—C17—C18—C19	−0.57 (13)
Cu—N1—C8—C9	40.63 (7)	C17—C18—C19—C20	0.26 (13)
C12—N2—C9—C8	159.78 (6)	C18—C19—C20—C15	0.83 (12)
C10—N2—C9—C8	−75.90 (7)	C16—C15—C20—C19	−1.60 (11)
Cu—N2—C9—C8	39.55 (7)	C14—C15—C20—C19	176.42 (7)
N1—C8—C9—N2	−52.20 (8)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O3	0.82 (1)	1.98 (1)	2.7641 (9)	161 (2)
O1*W*—H1*W*2···O2*W*^{i}	0.82 (1)	2.07 (1)	2.8871 (10)	172 (2)
O2*W*—H2*W*1···O1	0.83 (1)	2.08 (1)	2.8868 (9)	165 (2)
O2*W*—H2*W*2···O1*W*	0.83 (1)	2.12 (1)	2.9378 (11)	175 (2)

Symmetry code: (i) −*x*+1, *y*+1/2, −*z*+1/2.

[(*E*)-2-({[2-(Diethylamino)ethyl]imino}methyl)phenolato-κ^3N,N',O](2-phenylacetato-κ^2O,O')copper(II) (2)

Crystal data

$[Cu(C_8H_7O_2)(C_{13}H_{19}N_2O)]$
M_r = 417.98
Orthorhombic, $Pca2_1$
a = 23.1862 (10) Å
b = 6.4178 (3) Å
c = 13.1598 (6) Å
V = 1958.22 (15) Å^3
Z = 4
F(000) = 876
D_x = 1.418 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6436 reflections
θ = 3.9–33.6°
μ = 1.14 mm^{-1}
T = 100 K
Plate, blue
0.20 × 0.11 × 0.03 mm

Data collection

Rigaku OD SuperNova Dual source diffractometer with an Atlas detector
Radiation source: micro-focus sealed X-ray tube
Detector resolution: 10.6501 pixels mm^{-1}
ω scans
Absorption correction: gaussian CrysAlis PRO (Rigaku OD, 2018) Numerical absorption correction based on gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min} = 0.684, T_{max} = 1.000
46196 measured reflections
11501 independent reflections
7093 reflections with $I > 2\sigma(I)$
R_{int} = 0.089
θ_{max} = 41.3°, θ_{min} = 3.5°
h = −37→42
k = −11→11
l = −23→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.121$
$S = 1.04$
11501 reflections
245 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.20$ e Å^{-3}
$\Delta\rho_{min} = -1.04$ e Å^{-3}
Absolute structure: Flack *x* determined using 1976 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.035 (10)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu	0.50251 (2)	0.67151 (4)	0.58234 (5)	0.01478 (6)
O1	0.55832 (9)	0.8376 (3)	0.51299 (18)	0.0204 (4)
O2	0.44362 (8)	0.8849 (3)	0.55955 (16)	0.0185 (4)
O3	0.43374 (10)	0.6755 (3)	0.42593 (18)	0.0219 (5)
N1	0.55334 (9)	0.4358 (3)	0.5937 (2)	0.0180 (5)
N2	0.45221 (10)	0.5167 (4)	0.68793 (19)	0.0176 (4)
C1	0.61121 (12)	0.7875 (4)	0.4914 (2)	0.0167 (5)
C2	0.64665 (13)	0.9369 (5)	0.4416 (2)	0.0186 (5)
H2A	0.630815	1.069146	0.425069	0.022*
C3	0.70285 (13)	0.8961 (5)	0.4169 (2)	0.0201 (5)
H3A	0.725123	1.000151	0.383750	0.024*
C4	0.72806 (13)	0.7032 (5)	0.4396 (2)	0.0215 (6)
H4A	0.767133	0.675768	0.422466	0.026*
C5	0.69497 (12)	0.5539 (5)	0.4874 (2)	0.0200 (5)
H5A	0.711564	0.422133	0.502459	0.024*
C6	0.63715 (12)	0.5921 (5)	0.5145 (2)	0.0176 (5)
C7	0.60647 (11)	0.4276 (4)	0.5657 (2)	0.0181 (6)
H7A	0.627107	0.303159	0.580009	0.022*
C8	0.52631 (13)	0.2571 (5)	0.6443 (3)	0.0224 (6)
H8A	0.556181	0.164060	0.673164	0.027*
H8B	0.502894	0.176370	0.595273	0.027*
C9	0.48849 (14)	0.3425 (5)	0.7279 (3)	0.0226 (6)
H9A	0.463338	0.230491	0.754515	0.027*
H9B	0.512849	0.393847	0.784358	0.027*
C10	0.43476 (15)	0.6603 (5)	0.7715 (3)	0.0222 (6)
H10A	0.415201	0.578917	0.825322	0.027*
H10B	0.406761	0.762946	0.744670	0.027*
C11	0.48557 (16)	0.7759 (6)	0.8177 (3)	0.0283 (7)

H11A	0.471804	0.867734	0.872038	0.043*
H11B	0.513054	0.675182	0.845802	0.043*
H11C	0.504613	0.859261	0.765128	0.043*
C12	0.40028 (13)	0.4385 (5)	0.6321 (2)	0.0222 (6)
H12A	0.413673	0.356314	0.572965	0.027*
H12B	0.378887	0.560191	0.605402	0.027*
C13	0.35861 (15)	0.3051 (6)	0.6926 (3)	0.0319 (8)
H13A	0.324823	0.272829	0.650745	0.048*
H13B	0.346350	0.381139	0.753507	0.048*
H13C	0.377714	0.175336	0.712744	0.048*
C14	0.42161 (12)	0.8351 (5)	0.4727 (2)	0.0170 (5)
C15	0.37829 (13)	0.9942 (5)	0.4325 (2)	0.0215 (6)
H15A	0.351429	1.028904	0.488492	0.026*
H15B	0.399690	1.123004	0.415505	0.026*
C16	0.34295 (12)	0.9344 (5)	0.3416 (2)	0.0192 (5)
C17	0.33190 (13)	1.0802 (5)	0.2656 (2)	0.0212 (6)
H17A	0.350911	1.211234	0.267692	0.025*
C18	0.29376 (14)	1.0383 (6)	0.1867 (3)	0.0258 (6)
H18A	0.286285	1.140770	0.136301	0.031*
C19	0.26675 (14)	0.8464 (6)	0.1823 (3)	0.0278 (7)
H19A	0.240039	0.817626	0.129361	0.033*
C20	0.27865 (15)	0.6955 (6)	0.2551 (3)	0.0275 (7)
H20A	0.260772	0.562618	0.250909	0.033*
C21	0.31655 (13)	0.7385 (5)	0.3340 (3)	0.0226 (6)
H21A	0.324698	0.634210	0.383164	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.01389 (12)	0.01448 (11)	0.01595 (12)	0.00064 (11)	0.00013 (14)	0.00139 (17)
O1	0.0152 (9)	0.0202 (10)	0.0257 (11)	0.0031 (7)	0.0032 (8)	0.0053 (8)
O2	0.0156 (8)	0.0208 (10)	0.0191 (11)	0.0012 (7)	−0.0011 (7)	0.0018 (7)
O3	0.0217 (10)	0.0242 (11)	0.0197 (11)	0.0051 (8)	0.0012 (8)	−0.0013 (8)
N1	0.0176 (9)	0.0150 (9)	0.0214 (14)	−0.0002 (7)	0.0000 (9)	0.0003 (9)
N2	0.0165 (10)	0.0200 (11)	0.0165 (11)	−0.0005 (8)	0.0008 (8)	0.0026 (9)
C1	0.0169 (12)	0.0184 (12)	0.0148 (12)	0.0005 (9)	−0.0008 (9)	0.0001 (9)
C2	0.0173 (12)	0.0192 (13)	0.0192 (13)	0.0007 (10)	0.0010 (9)	0.0000 (10)
C3	0.0175 (13)	0.0249 (14)	0.0178 (14)	−0.0032 (10)	0.0012 (10)	−0.0004 (11)
C4	0.0161 (13)	0.0275 (16)	0.0210 (14)	0.0014 (10)	0.0037 (10)	−0.0019 (11)
C5	0.0174 (13)	0.0202 (14)	0.0226 (14)	0.0035 (10)	0.0011 (10)	−0.0011 (11)
C6	0.0162 (12)	0.0182 (13)	0.0186 (13)	0.0005 (9)	−0.0015 (9)	−0.0016 (10)
C7	0.0171 (11)	0.0148 (11)	0.0225 (16)	0.0022 (8)	−0.0020 (9)	−0.0017 (10)
C8	0.0204 (14)	0.0187 (14)	0.0281 (16)	−0.0010 (11)	0.0003 (11)	0.0025 (12)
C9	0.0237 (14)	0.0216 (15)	0.0227 (15)	0.0014 (11)	0.0015 (11)	0.0057 (11)
C10	0.0245 (15)	0.0240 (16)	0.0180 (14)	0.0005 (12)	0.0042 (11)	0.0002 (11)
C11	0.0327 (17)	0.0254 (16)	0.0269 (18)	−0.0012 (13)	0.0006 (13)	−0.0014 (13)
C12	0.0192 (13)	0.0270 (15)	0.0205 (15)	−0.0046 (11)	−0.0002 (10)	0.0010 (12)
C13	0.0255 (17)	0.038 (2)	0.0323 (19)	−0.0116 (14)	0.0027 (14)	0.0040 (15)

C14	0.0127 (11)	0.0224 (13)	0.0160 (12)	0.0005 (9)	0.0020 (8)	0.0042 (10)
C15	0.0208 (14)	0.0203 (14)	0.0234 (15)	0.0027 (10)	−0.0039 (11)	0.0018 (11)
C16	0.0154 (12)	0.0226 (14)	0.0196 (14)	0.0018 (10)	−0.0002 (10)	0.0026 (10)
C17	0.0164 (13)	0.0243 (15)	0.0228 (15)	0.0026 (11)	0.0031 (10)	0.0049 (11)
C18	0.0254 (15)	0.0350 (18)	0.0170 (14)	0.0087 (13)	0.0026 (11)	0.0055 (12)
C19	0.0232 (15)	0.041 (2)	0.0193 (15)	0.0076 (13)	−0.0038 (11)	−0.0079 (13)
C20	0.0245 (16)	0.0287 (18)	0.0294 (18)	0.0011 (12)	−0.0019 (13)	−0.0047 (13)
C21	0.0214 (13)	0.0220 (14)	0.0244 (15)	0.0003 (11)	−0.0015 (12)	0.0021 (12)

Geometric parameters (Å, º)

Cu—O1	1.909 (2)	C9—H9B	0.9900
Cu—N1	1.923 (2)	C10—C11	1.519 (5)
Cu—O2	1.957 (2)	C10—H10A	0.9900
Cu—N2	2.068 (2)	C10—H10B	0.9900
Cu—O3	2.604 (2)	C11—H11A	0.9800
O1—C1	1.299 (3)	C11—H11B	0.9800
O2—C14	1.292 (4)	C11—H11C	0.9800
O3—C14	1.228 (4)	C12—C13	1.517 (4)
N1—C7	1.287 (3)	C12—H12A	0.9900
N1—C8	1.467 (4)	C12—H12B	0.9900
N2—C10	1.490 (4)	C13—H13A	0.9800
N2—C9	1.495 (4)	C13—H13B	0.9800
N2—C12	1.497 (4)	C13—H13C	0.9800
C1—C2	1.423 (4)	C14—C15	1.526 (4)
C1—C6	1.424 (4)	C15—C16	1.500 (4)
C2—C3	1.368 (4)	C15—H15A	0.9900
C2—H2A	0.9500	C15—H15B	0.9900
C3—C4	1.402 (4)	C16—C17	1.394 (4)
C3—H3A	0.9500	C16—C21	1.402 (4)
C4—C5	1.379 (4)	C17—C18	1.390 (5)
C4—H4A	0.9500	C17—H17A	0.9500
C5—C6	1.408 (4)	C18—C19	1.383 (5)
C5—H5A	0.9500	C18—H18A	0.9500
C6—C7	1.441 (4)	C19—C20	1.390 (5)
C7—H7A	0.9500	C19—H19A	0.9500
C8—C9	1.509 (5)	C20—C21	1.387 (5)
C8—H8A	0.9900	C20—H20A	0.9500
C8—H8B	0.9900	C21—H21A	0.9500
C9—H9A	0.9900		

O1—Cu—N1	93.49 (9)	C8—C9—H9B	109.7
O1—Cu—O2	90.51 (9)	H9A—C9—H9B	108.2
N1—Cu—O2	171.79 (10)	N2—C10—C11	112.8 (3)
O1—Cu—N2	166.33 (11)	N2—C10—H10A	109.0
N1—Cu—N2	85.17 (10)	C11—C10—H10A	109.0
O2—Cu—N2	92.61 (9)	N2—C10—H10B	109.0
O1—Cu—O3	91.81 (9)	C11—C10—H10B	109.0

N1—Cu—O3	116.37 (10)	H10A—C10—H10B	107.8
O2—Cu—O3	56.27 (8)	C10—C11—H11A	109.5
N2—Cu—O3	100.98 (9)	C10—C11—H11B	109.5
C1—O1—Cu	127.30 (19)	H11A—C11—H11B	109.5
C14—O2—Cu	103.79 (18)	C10—C11—H11C	109.5
C14—O3—Cu	75.67 (17)	H11A—C11—H11C	109.5
C7—N1—C8	120.5 (2)	H11B—C11—H11C	109.5
C7—N1—Cu	126.6 (2)	N2—C12—C13	116.4 (3)
C8—N1—Cu	112.84 (18)	N2—C12—H12A	108.2
C10—N2—C9	110.8 (3)	C13—C12—H12A	108.2
C10—N2—C12	110.6 (2)	N2—C12—H12B	108.2
C9—N2—C12	112.0 (2)	C13—C12—H12B	108.2
C10—N2—Cu	110.60 (19)	H12A—C12—H12B	107.4
C9—N2—Cu	106.15 (18)	C12—C13—H13A	109.5
C12—N2—Cu	106.56 (18)	C12—C13—H13B	109.5
O1—C1—C2	118.6 (3)	H13A—C13—H13B	109.5
O1—C1—C6	124.8 (3)	C12—C13—H13C	109.5
C2—C1—C6	116.6 (3)	H13A—C13—H13C	109.5
C3—C2—C1	122.1 (3)	H13B—C13—H13C	109.5
C3—C2—H2A	119.0	O3—C14—O2	124.0 (3)
C1—C2—H2A	119.0	O3—C14—C15	122.4 (3)
C2—C3—C4	121.0 (3)	O2—C14—C15	113.6 (3)
C2—C3—H3A	119.5	C16—C15—C14	117.7 (3)
C4—C3—H3A	119.5	C16—C15—H15A	107.9
C5—C4—C3	118.6 (3)	C14—C15—H15A	107.9
C5—C4—H4A	120.7	C16—C15—H15B	107.9
C3—C4—H4A	120.7	C14—C15—H15B	107.9
C4—C5—C6	121.6 (3)	H15A—C15—H15B	107.2
C4—C5—H5A	119.2	C17—C16—C21	118.0 (3)
C6—C5—H5A	119.2	C17—C16—C15	120.1 (3)
C5—C6—C1	120.1 (3)	C21—C16—C15	121.7 (3)
C5—C6—C7	117.4 (3)	C18—C17—C16	121.6 (3)
C1—C6—C7	122.4 (3)	C18—C17—H17A	119.2
N1—C7—C6	125.2 (3)	C16—C17—H17A	119.2
N1—C7—H7A	117.4	C19—C18—C17	119.5 (3)
C6—C7—H7A	117.4	C19—C18—H18A	120.3
N1—C8—C9	107.2 (3)	C17—C18—H18A	120.3
N1—C8—H8A	110.3	C18—C19—C20	120.1 (3)
C9—C8—H8A	110.3	C18—C19—H19A	120.0
N1—C8—H8B	110.3	C20—C19—H19A	120.0
C9—C8—H8B	110.3	C21—C20—C19	120.2 (3)
H8A—C8—H8B	108.5	C21—C20—H20A	119.9
N2—C9—C8	110.0 (3)	C19—C20—H20A	119.9
N2—C9—H9A	109.7	C20—C21—C16	120.6 (3)
C8—C9—H9A	109.7	C20—C21—H21A	119.7
N2—C9—H9B	109.7	C16—C21—H21A	119.7
Cu—O1—C1—C2	−178.1 (2)	C9—N2—C10—C11	66.1 (3)

Cu—O1—C1—C6	1.5 (4)	C12—N2—C10—C11	−169.2 (3)
O1—C1—C2—C3	179.7 (3)	Cu—N2—C10—C11	−51.4 (3)
C6—C1—C2—C3	0.0 (4)	C10—N2—C12—C13	−64.0 (4)
C1—C2—C3—C4	0.1 (5)	C9—N2—C12—C13	60.1 (4)
C2—C3—C4—C5	0.2 (5)	Cu—N2—C12—C13	175.8 (3)
C3—C4—C5—C6	−0.7 (5)	Cu—O3—C14—O2	−4.8 (2)
C4—C5—C6—C1	0.8 (5)	Cu—O3—C14—C15	175.4 (3)
C4—C5—C6—C7	−179.0 (3)	Cu—O2—C14—O3	6.4 (3)
O1—C1—C6—C5	179.9 (3)	Cu—O2—C14—C15	−173.84 (19)
C2—C1—C6—C5	−0.5 (4)	O3—C14—C15—C16	10.0 (4)
O1—C1—C6—C7	−0.4 (5)	O2—C14—C15—C16	−169.8 (3)
C2—C1—C6—C7	179.3 (3)	C14—C15—C16—C17	−139.8 (3)
C8—N1—C7—C6	179.2 (3)	C14—C15—C16—C21	45.1 (4)
Cu—N1—C7—C6	−4.0 (4)	C21—C16—C17—C18	3.1 (5)
C5—C6—C7—N1	−178.5 (3)	C15—C16—C17—C18	−172.1 (3)
C1—C6—C7—N1	1.7 (5)	C16—C17—C18—C19	−1.2 (5)
C7—N1—C8—C9	139.9 (3)	C17—C18—C19—C20	−1.2 (5)
Cu—N1—C8—C9	−37.3 (3)	C18—C19—C20—C21	1.6 (5)
C10—N2—C9—C8	−155.3 (3)	C19—C20—C21—C16	0.5 (5)
C12—N2—C9—C8	80.7 (3)	C17—C16—C21—C20	−2.8 (5)
Cu—N2—C9—C8	−35.2 (3)	C15—C16—C21—C20	172.4 (3)
N1—C8—C9—N2	47.6 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*B*···O2^{i}	0.99	2.37	3.260 (4)	149
C9—H9*B*···O3^{ii}	0.99	2.28	3.172 (4)	149
C12—H12*B*···O2	0.99	2.64	3.183 (4)	115

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1, −*y*+1, *z*+1/2.

Bis[*μ*-(*E*)-2-({[3-(diethylamino)propyl]imino}methyl)phenolato]-$\kappa^4N,N',O:O;\kappa^4O:N,N',O$-(*μ*-2-methylbenzoato-$\kappa^2O:O'$)copper(II) perchlorate (3)

Crystal data

$[Cu_2(C_8H_7O_2)(C_{12}H_{17}N_2O)_2]ClO_4$
M_r = 772.22
Orthorhombic, *Pbca*
a = 10.51085 (16) Å
b = 22.2419 (5) Å
c = 28.8403 (5) Å
V = 6742.3 (2) Å^3
Z = 8
F(000) = 3200
D_x = 1.521 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 21097 reflections
θ = 3.7–36.4°
μ = 1.40 mm^{-1}
T = 100 K
Plate, green-blue
0.26 × 0.21 × 0.03 mm

Data collection

Rigaku OD SuperNova Dual source diffractometer with an Atlas detector
Radiation source: micro-focus sealed X-ray tube
Detector resolution: 10.6501 pixels mm^{-1}
ω scans
Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2018)
T_{min} = 0.614, T_{max} = 1.000

154652 measured reflections
22070 independent reflections
12413 reflections with $I > 2\sigma(I)$
$R_{int} = 0.090$
$\theta_{max} = 41.6°$, $\theta_{min} = 3.4°$
$h = -18 \rightarrow 19$
$k = -33 \rightarrow 40$
$l = -35 \rightarrow 52$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.135$
$S = 1.03$
22070 reflections
467 parameters
44 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 5.3824P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.13$ e Å^{-3}
$\Delta\rho_{min} = -1.10$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.28173 (2)	1.08502 (2)	0.16413 (2)	0.01838 (4)	
Cu2	0.32761 (2)	0.99599 (2)	0.08706 (2)	0.01958 (4)	
O1	0.18853 (12)	1.01143 (6)	0.14771 (5)	0.0219 (2)	
O2	0.44003 (11)	1.05731 (6)	0.11374 (5)	0.0215 (2)	
O3	0.18608 (13)	1.12125 (6)	0.11331 (5)	0.0241 (3)	
O4	0.24510 (13)	1.06268 (6)	0.05351 (5)	0.0255 (3)	
N1	0.32825 (14)	1.17468 (7)	0.18137 (6)	0.0223 (3)	
N2	0.35486 (14)	1.04593 (7)	0.21946 (5)	0.0229 (3)	
N3	0.42640 (14)	0.93093 (7)	0.11619 (6)	0.0232 (3)	
N4	0.24861 (19)	0.93856 (9)	0.03741 (7)	0.0353 (4)	
C1	0.15786 (15)	0.96685 (8)	0.17591 (6)	0.0204 (3)	
C2	0.06056 (16)	0.92586 (8)	0.16282 (8)	0.0259 (3)	
H2A	0.018193	0.931168	0.134018	0.031*	
C3	0.02630 (19)	0.87838 (9)	0.19118 (9)	0.0326 (4)	
H3A	−0.040146	0.852123	0.181767	0.039*	
C4	0.0877 (2)	0.86842 (10)	0.23339 (9)	0.0377 (5)	
H4A	0.063932	0.835617	0.252624	0.045*	
C5	0.1835 (2)	0.90699 (10)	0.24663 (8)	0.0340 (4)	
H5A	0.226834	0.900052	0.275026	0.041*	
C6	0.21861 (18)	0.95663 (8)	0.21897 (7)	0.0238 (3)	
C7	0.31918 (17)	0.99510 (8)	0.23622 (7)	0.0235 (3)	
H7A	0.363661	0.981258	0.262830	0.028*	
C8	0.45833 (19)	1.07664 (10)	0.24478 (7)	0.0305 (4)	
H8A	0.535325	1.078379	0.225058	0.037*	
H8B	0.479509	1.053689	0.273162	0.037*	
C9	0.4179 (2)	1.13985 (10)	0.25785 (7)	0.0310 (4)	

H9A	0.328741	1.138993	0.268907	0.037*
H9B	0.471883	1.154315	0.283668	0.037*
C10	0.42827 (18)	1.18331 (10)	0.21765 (7)	0.0297 (4)
H10A	0.422390	1.224879	0.229733	0.036*
H10B	0.512998	1.178625	0.203100	0.036*
C11	0.20745 (19)	1.20172 (11)	0.19811 (8)	0.0338 (5)
H11A	0.220059	1.244773	0.203678	0.051*
H11B	0.181586	1.182086	0.227028	0.051*
H11C	0.141026	1.196136	0.174653	0.051*
C12	0.3685 (2)	1.21036 (10)	0.14034 (8)	0.0314 (4)
H12A	0.390609	1.251243	0.150133	0.047*
H12B	0.298717	1.212011	0.117853	0.047*
H12C	0.442856	1.191360	0.125973	0.047*
C13	0.56329 (16)	1.04925 (8)	0.12129 (6)	0.0195 (3)
C14	0.64547 (17)	1.09933 (8)	0.12300 (7)	0.0232 (3)
H14A	0.611230	1.138621	0.119659	0.028*
C15	0.77541 (17)	1.09226 (9)	0.12948 (7)	0.0243 (3)
H15A	0.828659	1.126763	0.130131	0.029*
C16	0.82929 (17)	1.03539 (9)	0.13505 (8)	0.0273 (4)
H16A	0.918577	1.030819	0.138755	0.033*
C17	0.75007 (18)	0.98594 (9)	0.13505 (8)	0.0276 (4)
H17A	0.785487	0.947130	0.139803	0.033*
C18	0.61758 (16)	0.99162 (8)	0.12815 (6)	0.0216 (3)
C19	0.54316 (17)	0.93722 (8)	0.12929 (7)	0.0247 (3)
H19A	0.584320	0.902305	0.140915	0.030*
C20	0.37186 (19)	0.87002 (9)	0.12140 (8)	0.0295 (4)
H20A	0.294207	0.872019	0.140770	0.035*
H20B	0.433996	0.843546	0.137170	0.035*
C21	0.3391 (2)	0.84414 (11)	0.07424 (11)	0.0425 (6)
H21A	0.414251	0.847807	0.053734	0.051*
H21B	0.319906	0.800810	0.077773	0.051*
C22	0.2275 (3)	0.87454 (11)	0.05142 (10)	0.0431 (6)
H22A	0.203933	0.851222	0.023480	0.052*
H22B	0.154364	0.873092	0.073008	0.052*
C23	0.3397 (3)	0.94346 (15)	−0.00141 (10)	0.0532 (7)
H23A	0.309784	0.919079	−0.027527	0.080*
H23B	0.423371	0.928975	0.008627	0.080*
H23C	0.346501	0.985575	−0.011092	0.080*
C24	0.1215 (3)	0.95918 (14)	0.02074 (11)	0.0534 (7)
H24A	0.089533	0.931073	−0.002688	0.080*
H24B	0.129479	0.999341	0.007071	0.080*
H24C	0.062063	0.960663	0.046891	0.080*
C25	0.19144 (16)	1.10812 (8)	0.07068 (6)	0.0209 (3)
C26	0.12577 (17)	1.15150 (8)	0.03844 (6)	0.0220 (3)
C27	0.02568 (18)	1.18557 (9)	0.05705 (7)	0.0259 (3)
H27A	0.003035	1.180622	0.088715	0.031*
C28	−0.0408 (2)	1.22642 (10)	0.02983 (8)	0.0333 (4)
H28A	−0.110083	1.248384	0.042477	0.040*

C29	−0.0050 (2)	1.23482 (10)	−0.01588 (9)	0.0388 (5)	
H29A	−0.048923	1.263227	−0.034560	0.047*	
C30	0.0943 (2)	1.20205 (11)	−0.03445 (8)	0.0358 (5)	
H30A	0.117859	1.208614	−0.065840	0.043*	
C31	0.16139 (19)	1.15931 (9)	−0.00827 (7)	0.0277 (4)	
C32	0.2693 (2)	1.12608 (12)	−0.03120 (8)	0.0384 (5)	
H32A	0.290621	1.145716	−0.060613	0.058*	
H32B	0.243726	1.084418	−0.037115	0.058*	
H32C	0.343858	1.126512	−0.010781	0.058*	
Cl1	0.71528 (4)	0.76845 (2)	0.15982 (2)	0.02309 (8)	
O11A	0.7359 (13)	0.8310 (3)	0.1481 (5)	0.0305 (14)	0.64 (4)
O12A	0.5835 (7)	0.7574 (6)	0.1677 (4)	0.0448 (17)	0.64 (4)
O13A	0.7872 (10)	0.7544 (7)	0.2006 (4)	0.054 (2)	0.64 (4)
O14A	0.7590 (13)	0.7325 (4)	0.1220 (4)	0.059 (2)	0.64 (4)
O11B	0.752 (2)	0.8298 (6)	0.1535 (9)	0.030 (2)	0.36 (4)
O12B	0.5852 (13)	0.7673 (13)	0.1760 (10)	0.058 (5)	0.36 (4)
O13B	0.7955 (17)	0.7392 (9)	0.1922 (7)	0.053 (3)	0.36 (4)
O14B	0.722 (3)	0.7377 (9)	0.1163 (5)	0.068 (4)	0.36 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02042 (9)	0.01657 (9)	0.01815 (8)	−0.00045 (7)	−0.00320 (7)	−0.00008 (7)
Cu2	0.01951 (9)	0.01557 (9)	0.02365 (10)	0.00206 (7)	−0.00306 (7)	−0.00206 (7)
O1	0.0221 (5)	0.0193 (6)	0.0244 (6)	−0.0017 (4)	−0.0033 (4)	−0.0001 (5)
O2	0.0177 (5)	0.0171 (6)	0.0296 (6)	0.0018 (4)	−0.0019 (4)	−0.0030 (5)
O3	0.0316 (6)	0.0205 (6)	0.0203 (6)	0.0060 (5)	−0.0060 (5)	−0.0016 (5)
O4	0.0320 (6)	0.0224 (6)	0.0221 (6)	0.0068 (5)	−0.0036 (5)	−0.0010 (5)
N1	0.0204 (6)	0.0199 (7)	0.0266 (7)	−0.0024 (5)	0.0026 (5)	−0.0039 (5)
N2	0.0220 (6)	0.0246 (8)	0.0221 (7)	−0.0023 (5)	−0.0050 (5)	0.0014 (5)
N3	0.0204 (6)	0.0166 (6)	0.0326 (8)	0.0014 (5)	−0.0028 (5)	−0.0002 (6)
N4	0.0414 (10)	0.0278 (9)	0.0367 (10)	−0.0033 (7)	−0.0122 (8)	−0.0086 (8)
C1	0.0184 (7)	0.0159 (7)	0.0269 (8)	0.0019 (5)	0.0015 (6)	−0.0010 (6)
C2	0.0187 (7)	0.0201 (8)	0.0388 (10)	0.0010 (6)	−0.0001 (7)	−0.0048 (7)
C3	0.0257 (8)	0.0181 (9)	0.0539 (13)	−0.0036 (6)	0.0070 (8)	−0.0052 (8)
C4	0.0469 (12)	0.0214 (10)	0.0449 (13)	−0.0063 (8)	0.0116 (10)	0.0046 (9)
C5	0.0463 (12)	0.0223 (9)	0.0333 (10)	−0.0012 (8)	0.0021 (9)	0.0057 (8)
C6	0.0266 (8)	0.0182 (8)	0.0266 (8)	0.0004 (6)	0.0000 (6)	0.0029 (6)
C7	0.0263 (8)	0.0209 (8)	0.0234 (7)	0.0009 (6)	−0.0046 (6)	0.0031 (6)
C8	0.0257 (8)	0.0383 (12)	0.0273 (9)	−0.0082 (7)	−0.0091 (7)	0.0042 (8)
C9	0.0307 (9)	0.0371 (11)	0.0253 (9)	−0.0117 (8)	−0.0039 (7)	−0.0058 (8)
C10	0.0251 (8)	0.0297 (10)	0.0343 (10)	−0.0091 (7)	−0.0013 (7)	−0.0045 (8)
C11	0.0246 (8)	0.0384 (12)	0.0383 (11)	0.0001 (8)	0.0053 (8)	−0.0165 (9)
C12	0.0315 (9)	0.0228 (9)	0.0399 (11)	0.0001 (7)	0.0057 (8)	0.0068 (8)
C13	0.0198 (6)	0.0180 (7)	0.0207 (7)	0.0006 (5)	−0.0001 (5)	−0.0011 (5)
C14	0.0215 (7)	0.0190 (8)	0.0291 (8)	−0.0001 (6)	0.0005 (6)	−0.0031 (6)
C15	0.0208 (7)	0.0238 (9)	0.0282 (8)	−0.0026 (6)	0.0001 (6)	−0.0037 (7)
C16	0.0192 (7)	0.0260 (9)	0.0367 (10)	−0.0003 (6)	−0.0047 (7)	−0.0010 (7)

C17	0.0221 (7)	0.0228 (9)	0.0380 (10)	0.0017 (6)	−0.0064 (7)	0.0031 (7)
C18	0.0199 (7)	0.0188 (8)	0.0261 (8)	0.0016 (5)	−0.0033 (6)	0.0013 (6)
C19	0.0231 (7)	0.0173 (8)	0.0336 (9)	0.0034 (6)	−0.0028 (6)	0.0025 (7)
C20	0.0240 (8)	0.0161 (8)	0.0484 (12)	0.0015 (6)	−0.0005 (8)	0.0024 (8)
C21	0.0417 (12)	0.0216 (10)	0.0643 (17)	−0.0029 (8)	0.0073 (11)	−0.0096 (10)
C22	0.0471 (13)	0.0308 (12)	0.0514 (15)	−0.0087 (10)	−0.0051 (11)	−0.0138 (11)
C23	0.0700 (19)	0.0531 (18)	0.0365 (13)	−0.0012 (14)	0.0041 (13)	−0.0218 (12)
C24	0.0475 (14)	0.0573 (18)	0.0553 (16)	−0.0143 (13)	−0.0279 (13)	0.0002 (14)
C25	0.0232 (7)	0.0175 (7)	0.0221 (7)	0.0004 (5)	−0.0037 (6)	0.0010 (6)
C26	0.0249 (7)	0.0184 (8)	0.0227 (7)	−0.0014 (6)	−0.0050 (6)	0.0029 (6)
C27	0.0275 (8)	0.0199 (8)	0.0303 (9)	0.0012 (6)	−0.0056 (7)	0.0012 (7)
C28	0.0336 (10)	0.0224 (9)	0.0440 (12)	0.0036 (7)	−0.0117 (9)	0.0037 (8)
C29	0.0462 (12)	0.0262 (11)	0.0439 (12)	0.0001 (9)	−0.0183 (10)	0.0131 (9)
C30	0.0474 (12)	0.0314 (11)	0.0287 (10)	−0.0057 (9)	−0.0092 (9)	0.0105 (8)
C31	0.0333 (9)	0.0251 (9)	0.0249 (8)	−0.0049 (7)	−0.0045 (7)	0.0045 (7)
C32	0.0481 (13)	0.0394 (13)	0.0277 (10)	0.0012 (10)	0.0058 (9)	0.0043 (9)
Cl1	0.02552 (18)	0.01891 (18)	0.02484 (18)	0.00209 (14)	−0.00050 (14)	0.00546 (14)
O11A	0.040 (4)	0.0144 (16)	0.037 (3)	0.0024 (15)	−0.008 (3)	0.0036 (14)
O12A	0.026 (2)	0.051 (4)	0.057 (3)	−0.010 (2)	−0.0030 (17)	0.013 (2)
O13A	0.040 (3)	0.069 (5)	0.052 (3)	−0.001 (3)	−0.013 (2)	0.037 (3)
O14A	0.092 (5)	0.0242 (19)	0.060 (4)	0.003 (3)	0.038 (3)	−0.010 (3)
O11B	0.031 (4)	0.018 (3)	0.041 (6)	0.001 (3)	−0.015 (3)	0.000 (3)
O12B	0.026 (4)	0.056 (8)	0.092 (11)	0.007 (4)	0.008 (5)	0.019 (7)
O13B	0.042 (4)	0.050 (6)	0.066 (7)	0.020 (4)	−0.016 (4)	0.025 (5)
O14B	0.135 (12)	0.036 (6)	0.033 (4)	−0.032 (7)	−0.001 (6)	−0.010 (3)

Geometric parameters (Å, º)

Cu1—O3	1.9514 (13)	C12—H12C	0.9800
Cu1—O1	1.9654 (13)	C13—C14	1.410 (2)
Cu1—N2	1.9731 (15)	C13—C18	1.417 (2)
Cu1—N1	2.1126 (16)	C14—C15	1.387 (2)
Cu1—O2	2.2935 (13)	C14—H14A	0.9500
Cu1—Cu2	3.0155 (3)	C15—C16	1.395 (3)
Cu2—O2	1.9615 (13)	C15—H15A	0.9500
Cu2—N3	1.9693 (15)	C16—C17	1.379 (3)
Cu2—O4	1.9719 (14)	C16—H16A	0.9500
Cu2—N4	2.0909 (18)	C17—C18	1.412 (3)
Cu2—O1	2.3053 (14)	C17—H17A	0.9500
O1—C1	1.322 (2)	C18—C19	1.441 (3)
O2—C13	1.326 (2)	C19—H19A	0.9500
O3—C25	1.265 (2)	C20—C21	1.517 (4)
O4—C25	1.259 (2)	C20—H20A	0.9900
N1—C11	1.485 (2)	C20—H20B	0.9900
N1—C12	1.486 (3)	C21—C22	1.505 (4)
N1—C10	1.496 (3)	C21—H21A	0.9900
N2—C7	1.285 (2)	C21—H21B	0.9900
N2—C8	1.477 (2)	C22—H22A	0.9900

N3—C19	1.292 (2)	C22—H22B	0.9900
N3—C20	1.479 (2)	C23—H23A	0.9800
N4—C23	1.478 (4)	C23—H23B	0.9800
N4—C24	1.492 (3)	C23—H23C	0.9800
N4—C22	1.497 (3)	C24—H24A	0.9800
C1—C6	1.415 (3)	C24—H24B	0.9800
C1—C2	1.421 (2)	C24—H24C	0.9800
C2—C3	1.383 (3)	C25—C26	1.507 (2)
C2—H2A	0.9500	C26—C27	1.403 (3)
C3—C4	1.396 (4)	C26—C31	1.409 (3)
C3—H3A	0.9500	C27—C28	1.389 (3)
C4—C5	1.376 (3)	C27—H27A	0.9500
C4—H4A	0.9500	C28—C29	1.383 (4)
C5—C6	1.411 (3)	C28—H28A	0.9500
C5—H5A	0.9500	C29—C30	1.381 (4)
C6—C7	1.448 (3)	C29—H29A	0.9500
C7—H7A	0.9500	C30—C31	1.404 (3)
C8—C9	1.516 (3)	C30—H30A	0.9500
C8—H8A	0.9900	C31—C32	1.507 (3)
C8—H8B	0.9900	C32—H32A	0.9800
C9—C10	1.513 (3)	C32—H32B	0.9800
C9—H9A	0.9900	C32—H32C	0.9800
C9—H9B	0.9900	Cl1—O13B	1.417 (11)
C10—H10A	0.9900	Cl1—O12A	1.425 (7)
C10—H10B	0.9900	Cl1—O11B	1.428 (12)
C11—H11A	0.9800	Cl1—O14A	1.430 (6)
C11—H11B	0.9800	Cl1—O14B	1.433 (11)
C11—H11C	0.9800	Cl1—O13A	1.433 (7)
C12—H12A	0.9800	Cl1—O12B	1.445 (12)
C12—H12B	0.9800	Cl1—O11A	1.448 (7)

O3—Cu1—O1	84.62 (6)	H11A—C11—H11C	109.5
O3—Cu1—N2	171.91 (6)	H11B—C11—H11C	109.5
O1—Cu1—N2	91.26 (6)	N1—C12—H12A	109.5
O3—Cu1—N1	84.62 (6)	N1—C12—H12B	109.5
O1—Cu1—N1	163.37 (6)	H12A—C12—H12B	109.5
N2—Cu1—N1	97.79 (7)	N1—C12—H12C	109.5
O3—Cu1—O2	90.51 (5)	H12A—C12—H12C	109.5
O1—Cu1—O2	89.15 (5)	H12B—C12—H12C	109.5
N2—Cu1—O2	96.40 (6)	O2—C13—C14	119.83 (16)
N1—Cu1—O2	103.59 (5)	O2—C13—C18	122.59 (15)
O3—Cu1—Cu2	78.46 (4)	C14—C13—C18	117.58 (15)
O1—Cu1—Cu2	49.86 (4)	C15—C14—C13	121.20 (17)
N2—Cu1—Cu2	104.15 (5)	C15—C14—H14A	119.4
N1—Cu1—Cu2	139.14 (4)	C13—C14—H14A	119.4
O2—Cu1—Cu2	40.58 (3)	C14—C15—C16	121.19 (17)
O2—Cu2—N3	91.49 (6)	C14—C15—H15A	119.4
O2—Cu2—O4	86.24 (6)	C16—C15—H15A	119.4

N3—Cu2—O4	173.70 (6)	C17—C16—C15	118.55 (17)
O2—Cu2—N4	158.84 (7)	C17—C16—H16A	120.7
N3—Cu2—N4	93.01 (7)	C15—C16—H16A	120.7
O4—Cu2—N4	87.06 (7)	C16—C17—C18	121.59 (18)
O2—Cu2—O1	88.90 (5)	C16—C17—H17A	119.2
N3—Cu2—O1	96.90 (6)	C18—C17—H17A	119.2
O4—Cu2—O1	88.94 (5)	C17—C18—C13	119.84 (16)
N4—Cu2—O1	111.03 (7)	C17—C18—C19	117.18 (16)
O2—Cu2—Cu1	49.52 (4)	C13—C18—C19	122.97 (15)
N3—Cu2—Cu1	104.63 (5)	N3—C19—C18	126.86 (17)
O4—Cu2—Cu1	78.32 (4)	N3—C19—H19A	116.6
N4—Cu2—Cu1	147.40 (6)	C18—C19—H19A	116.6
O1—Cu2—Cu1	40.67 (3)	N3—C20—C21	110.15 (19)
C1—O1—Cu1	126.72 (12)	N3—C20—H20A	109.6
C1—O1—Cu2	120.64 (11)	C21—C20—H20A	109.6
Cu1—O1—Cu2	89.47 (5)	N3—C20—H20B	109.6
C13—O2—Cu2	123.99 (11)	C21—C20—H20B	109.6
C13—O2—Cu1	129.87 (11)	H20A—C20—H20B	108.1
Cu2—O2—Cu1	89.91 (5)	C22—C21—C20	113.5 (2)
C25—O3—Cu1	127.72 (12)	C22—C21—H21A	108.9
C25—O4—Cu2	127.43 (12)	C20—C21—H21A	108.9
C11—N1—C12	106.62 (17)	C22—C21—H21B	108.9
C11—N1—C10	108.75 (15)	C20—C21—H21B	108.9
C12—N1—C10	106.75 (15)	H21A—C21—H21B	107.7
C11—N1—Cu1	105.12 (12)	N4—C22—C21	115.5 (2)
C12—N1—Cu1	112.50 (13)	N4—C22—H22A	108.4
C10—N1—Cu1	116.64 (13)	C21—C22—H22A	108.4
C7—N2—C8	115.82 (16)	N4—C22—H22B	108.4
C7—N2—Cu1	125.31 (13)	C21—C22—H22B	108.4
C8—N2—Cu1	118.87 (13)	H22A—C22—H22B	107.5
C19—N3—C20	115.97 (16)	N4—C23—H23A	109.5
C19—N3—Cu2	123.10 (13)	N4—C23—H23B	109.5
C20—N3—Cu2	120.81 (12)	H23A—C23—H23B	109.5
C23—N4—C24	108.3 (2)	N4—C23—H23C	109.5
C23—N4—C22	111.8 (2)	H23A—C23—H23C	109.5
C24—N4—C22	104.3 (2)	H23B—C23—H23C	109.5
C23—N4—Cu2	102.51 (15)	N4—C24—H24A	109.5
C24—N4—Cu2	112.86 (16)	N4—C24—H24B	109.5
C22—N4—Cu2	117.07 (15)	H24A—C24—H24B	109.5
O1—C1—C6	123.39 (16)	N4—C24—H24C	109.5
O1—C1—C2	119.55 (17)	H24A—C24—H24C	109.5
C6—C1—C2	117.05 (17)	H24B—C24—H24C	109.5
C3—C2—C1	121.3 (2)	O4—C25—O3	125.98 (16)
C3—C2—H2A	119.3	O4—C25—C26	118.45 (16)
C1—C2—H2A	119.3	O3—C25—C26	115.56 (16)
C2—C3—C4	121.09 (19)	C27—C26—C31	119.90 (17)
C2—C3—H3A	119.5	C27—C26—C25	116.94 (16)
C4—C3—H3A	119.5	C31—C26—C25	123.16 (17)

C5—C4—C3	118.8 (2)	C28—C27—C26	120.9 (2)
C5—C4—H4A	120.6	C28—C27—H27A	119.5
C3—C4—H4A	120.6	C26—C27—H27A	119.5
C4—C5—C6	121.5 (2)	C29—C28—C27	119.4 (2)
C4—C5—H5A	119.3	C29—C28—H28A	120.3
C6—C5—H5A	119.3	C27—C28—H28A	120.3
C5—C6—C1	120.24 (18)	C30—C29—C28	120.2 (2)
C5—C6—C7	117.34 (18)	C30—C29—H29A	119.9
C1—C6—C7	122.41 (16)	C28—C29—H29A	119.9
N2—C7—C6	127.13 (17)	C29—C30—C31	121.9 (2)
N2—C7—H7A	116.4	C29—C30—H30A	119.0
C6—C7—H7A	116.4	C31—C30—H30A	119.0
N2—C8—C9	110.19 (16)	C30—C31—C26	117.7 (2)
N2—C8—H8A	109.6	C30—C31—C32	118.3 (2)
C9—C8—H8A	109.6	C26—C31—C32	124.01 (18)
N2—C8—H8B	109.6	C31—C32—H32A	109.5
C9—C8—H8B	109.6	C31—C32—H32B	109.5
H8A—C8—H8B	108.1	H32A—C32—H32B	109.5
C10—C9—C8	112.43 (17)	C31—C32—H32C	109.5
C10—C9—H9A	109.1	H32A—C32—H32C	109.5
C8—C9—H9A	109.1	H32B—C32—H32C	109.5
C10—C9—H9B	109.1	O13B—Cl1—O11B	111.3 (10)
C8—C9—H9B	109.1	O12A—Cl1—O14A	109.8 (5)
H9A—C9—H9B	107.8	O13B—Cl1—O14B	109.3 (9)
N1—C10—C9	113.79 (16)	O11B—Cl1—O14B	109.4 (11)
N1—C10—H10A	108.8	O12A—Cl1—O13A	110.1 (5)
C9—C10—H10A	108.8	O14A—Cl1—O13A	109.6 (5)
N1—C10—H10B	108.8	O13B—Cl1—O12B	110.0 (11)
C9—C10—H10B	108.8	O11B—Cl1—O12B	108.2 (11)
H10A—C10—H10B	107.7	O14B—Cl1—O12B	108.6 (9)
N1—C11—H11A	109.5	O12A—Cl1—O11A	110.4 (6)
N1—C11—H11B	109.5	O14A—Cl1—O11A	108.1 (6)
H11A—C11—H11B	109.5	O13A—Cl1—O11A	108.8 (5)
N1—C11—H11C	109.5		

Cu1—O1—C1—C6	−19.3 (2)	C16—C17—C18—C19	−179.3 (2)
Cu2—O1—C1—C6	96.02 (18)	O2—C13—C18—C17	178.64 (18)
Cu1—O1—C1—C2	161.71 (13)	C14—C13—C18—C17	−1.7 (3)
Cu2—O1—C1—C2	−82.93 (17)	O2—C13—C18—C19	−2.5 (3)
O1—C1—C2—C3	179.52 (17)	C14—C13—C18—C19	177.14 (18)
C6—C1—C2—C3	0.5 (3)	C20—N3—C19—C18	−179.53 (19)
C1—C2—C3—C4	−1.1 (3)	Cu2—N3—C19—C18	4.4 (3)
C2—C3—C4—C5	0.3 (3)	C17—C18—C19—N3	−167.3 (2)
C3—C4—C5—C6	1.2 (4)	C13—C18—C19—N3	13.8 (3)
C4—C5—C6—C1	−1.8 (3)	C19—N3—C20—C21	−115.9 (2)
C4—C5—C6—C7	179.1 (2)	Cu2—N3—C20—C21	60.3 (2)
O1—C1—C6—C5	−178.04 (18)	N3—C20—C21—C22	−70.2 (2)
C2—C1—C6—C5	0.9 (3)	C23—N4—C22—C21	69.0 (3)

O1—C1—C6—C7	1.0 (3)	C24—N4—C22—C21	−174.2 (2)
C2—C1—C6—C7	179.95 (17)	Cu2—N4—C22—C21	−48.7 (3)
C8—N2—C7—C6	178.45 (19)	C20—C21—C22—N4	67.0 (3)
Cu1—N2—C7—C6	−0.9 (3)	Cu2—O4—C25—O3	4.0 (3)
C5—C6—C7—N2	−171.1 (2)	Cu2—O4—C25—C26	−175.52 (12)
C1—C6—C7—N2	9.9 (3)	Cu1—O3—C25—O4	11.9 (3)
C7—N2—C8—C9	−125.45 (19)	Cu1—O3—C25—C26	−168.62 (12)
Cu1—N2—C8—C9	54.0 (2)	O4—C25—C26—C27	153.93 (18)
N2—C8—C9—C10	−79.2 (2)	O3—C25—C26—C27	−25.6 (2)
C11—N1—C10—C9	77.9 (2)	O4—C25—C26—C31	−26.8 (3)
C12—N1—C10—C9	−167.42 (18)	O3—C25—C26—C31	153.65 (18)
Cu1—N1—C10—C9	−40.7 (2)	C31—C26—C27—C28	1.1 (3)
C8—C9—C10—N1	72.8 (2)	C25—C26—C27—C28	−179.63 (18)
Cu2—O2—C13—C14	155.33 (13)	C26—C27—C28—C29	−1.9 (3)
Cu1—O2—C13—C14	−80.6 (2)	C27—C28—C29—C30	1.2 (3)
Cu2—O2—C13—C18	−25.1 (2)	C28—C29—C30—C31	0.4 (4)
Cu1—O2—C13—C18	99.03 (18)	C29—C30—C31—C26	−1.2 (3)
O2—C13—C14—C15	−178.08 (17)	C29—C30—C31—C32	−179.4 (2)
C18—C13—C14—C15	2.3 (3)	C27—C26—C31—C30	0.5 (3)
C13—C14—C15—C16	−0.7 (3)	C25—C26—C31—C30	−178.74 (18)
C14—C15—C16—C17	−1.5 (3)	C27—C26—C31—C32	178.5 (2)
C15—C16—C17—C18	2.0 (3)	C25—C26—C31—C32	−0.7 (3)
C16—C17—C18—C13	−0.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10*B*···O13*A*^{ai}	0.99	2.69	3.418 (12)	130
C10—H10*B*···O13*B*^{bi}	0.99	2.44	3.242 (14)	138
C11—H11*B*···O13*A*^{aii}	0.98	2.65	3.148 (8)	111
C11—H11*C*···O3	0.98	2.48	3.039 (2)	116
C12—H12*B*···O3	0.98	2.34	2.866 (3)	113
C14—H14*A*···O14*A*^{ai}	0.95	2.49	3.127 (10)	124
C19—H19*A*···O11*A*^{a}	0.95	2.26	3.159 (12)	158
C20—H20*B*···O12*A*^{a}	0.99	2.63	3.606 (13)	169
C24—H24*B*···O4	0.98	2.29	2.807 (3)	112

Symmetry codes: (i) −*x*+3/2, *y*+1/2, *z*; (ii) −*x*+1, *y*+1/2, −*z*+1/2.